VIBRONIC SPECTROSCOPY OF HETERO DIHALO-BENZYL RADICALS GENERATED BY CORONA DISCHARGE : JET-COOLED CHLOROFLUOROBENZYL RADICALS

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The technique of corona excited supersonic jet expansion coupled with a pinhole-type glass nozzle was applied to vibronic spectroscopy of jet-cooled chlorofluorobenzyl radicals for the vibronic assignments and measurements of electronic energies of the $D_1 \rightarrow D_0$ transition. The vibronic emission spectra were recorded with a long-path monochromator in the visible region. The 2,3-, 2,4-,[a] and 2,5-[b]chlorofluorobenzyl radicals were generated by corona discharge of corresponding precursor molecules, chlorofluorotoluenes seeded in a large amount of helium carrier gas. The emission spectra show the vibronic bands originating from two benzyl-type radicals, chlorofluorobenzyl and fluorobenzyl benzyl radicals, in which fluorobenzyl radicals were obtained by displacement of Cl by H atom produced by the dissociation of methyl C-H bond. From an analysis of the spectra observed, we could determine the electronic energies in $D_1 \rightarrow D_0$ transition and vibrational mode frequencies at the D_0 state of chlorofluorobenzyl radicals which show the origin band of the electronic transition to be shifted to red region, comparing with the parental benzyl radical. The red-shift is highly sensitive to the number, position, and kind of substituents in chlorofluorobenzyl radicals. From the quantitative analysis of the red-shift, it has been found that the additivity rule, discovered recently by Lee group predicts the observation very well. In addition, the negligible contribution of the substituent at the 4-position, the nodal point of the Hückel's molecular orbital theory, can be well describes by the disconnection of substituent from molecular plane of the benzene ring available for delocalized π electrons. In this presentation, I will discuss the spectroscopic observation of new chlorofluorobenzyl radicals and substituent effect on electronic transition energy which is useful for identification of isomeric substituted benzyl radicals.

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[a] C. S. Huh, Y. W. Yoon, and S. K. Lee, *J. Chem. Phys.* **136**, 174306 (2012).
[b] S. Y. Chae, Y. W. Yoon, and S. K. Lee, *Chem. Phys. Lett.* **612**, 134 (2014).